Exploring oxygen's influence

Managing director
Dan Johnson

By Paul Smith, Martin Day, Simon Schmidt, Jacqui McRae, Keren Bindon, Stella Kassara, Alex Schulkin, Radka Kolouchova, Eric Wilkes, Markus Herderich and Dan Johnson
The Australian Wine Research Institute, PO Box 197, Glen Osmond, SA 5064, Australia

There are a number of unanswered questions about oxygen's role in the winemaking process. How much oxygen gets into juice through production? What does juice exposure to oxygen do to final wine style and composition? What does oxygen exposure during fermentation do to wine style? Can oxygen be better measured during winemaking or markers for exposure be identified? This article presents results from the first stage of a research program at the AWRI investigating influences on wine style from management of oxygen during winemaking.

AT A GLANCE

- Knowledge about the influence of oxygen (O_2) during fermentation on wine composition and sensory properties is currently limited.
- A pilot-scale experiment investigated the effects of delivering three different gas treatments to Shiraz ferments: (1) air, (2) 40% oxygen/60% nitrogen and (3) 100% nitrogen (N_2). A control ferment received no gas delivery.
- Ferments treated with air or 40% O_2 completed alcoholic and malolactic fermentations more quickly than the N_2-treated or control ferments.
- Wines resulting from air or 40% O_2 treatments were found to have more stable pigments and smaller tannins; they also exhibited less astringency and bitterness.
- Wines exposed to air or O_2 during fermentation were less susceptible to oxidation by oxygen ingress through the bottle closure during 12 months' bottle ageing.
- Increased oxygen exposure during red winemaking may reduce the need for extended wine ageing, resulting in the less astringent mouthfeel characteristics usually associated with aged wines at a much earlier stage.
- This work forms part of a broader research program at the AWRI, investigating the impact of early oxygen exposure on wine style.

OXYGEN IN AUSTRALIAN WINEMAKING

The practice of winemaking in Australia has a tendency to focus on excluding oxygen, sometimes described as a 'reductive' winemaking style. Dry ice and sulfur dioxide (SO_2) are used liberally to protect grapes during crushing and pressing and juices during transfer. While serving to protect against the negative effects of oxidation, blanket application of these approaches may increase the risk of sulfidic off-characters and also unnecessarily limit the tools available to winemakers to manipulate wine style.

Consultation with industry indicates sporadic use of oxygen during primary fermentation, especially with red musts. Some wineries use air to minimise sulfidic (or 'reductive') aroma formation and other wineries use oxygen to help stabilise colour. There is limited scientific understanding of how these practices impact on wine and very little scientific research has been reported on the effects of oxygen use during fermentation on wine composition or sensory properties.

WHAT IS ALREADY KNOWN ABOUT THE EFFECTS OF OXYGEN DURING FERMENTATION?

Oxygen exposure occurs naturally to varying degrees through the production of grape juice during mechanical harvesting, crushing and pressing. Studies of inert juice pressing (using nitrogen gas blanketing during the operation of a tank/membrane press) and hyperoxidation (phenolic stabilisation by exposure to very large amounts of oxygen after pressing) have been reported (Boselli *et al.* 2010, Cejudo-Bastante *et al.* 2011). These treatments were found to affect juice phenolic composition in different ways, and the ▸

hyperoxidation treatment was also shown to cause decreases in important aroma compounds. However, these studies represent the extremes of winemaking practice and do not shed much light on the effects of more moderate oxygen exposure. Research into the role of oxygen in fermentation has generally been focussed on the stimulation of fermentation rates and assisting in the completion of difficult fermentations.

In terms of oxygen effects on wine composition, the limited literature shows that single dose oxygen exposure during fermentation can alter the ester profile, increase the production of higher alcohols and alter the volatile fatty acid composition compared with strictly anaerobic fermentations. Oxygen dose and duration have not been explored. The major project on wine and oxygen at the AWRI aims to study dose-controlled additions of oxygen and monitor effects on fermentation efficiency and wine composition. This report discusses the effects of oxygen on phenolics, metals and malolactic fermentation observed in a study conducted during the 2012 vintage.

CONTROLLED OXYGEN DELIVERY DURING RED WINE FERMENTATIONS

Shiraz wines (730kg batches) were made in triplicate using rotary fermenters each fitted with three stainless steel sintered sparging heads used to deliver gases during fermentation. The three gas treatments in the experiment were air (containing approximately 20% oxygen), a mixture of 40% oxygen and 60% nitrogen (O_240) and pure nitrogen (N_2). A control treatment received no gas addition at all. Fermentations were conducted at 25°C and a total of eight gas treatments were applied for 60 minutes every 12 hours, starting 24 hours after inoculation. Wine colour and tannin were measured after fermentation (time 0), and after two and 12 months' bottle ageing under two different screwcap liners, Saran Tin (ST) and Saranex (Sx).

ALCOHOLIC AND MALOLACTIC FERMENTATION EFFICIENCY

The air and O_240 treatments completed alcoholic fermentation five days after inoculation, one day earlier than the N_2 and control treatments. Throughout the fermentation, the number of viable yeast cells was similar across all treatments, suggesting that any differences between treatments were not related to biomass changes. Malolactic fermentation (MLF) was also more rapid in the air and O_240-treated wines (completed in eight days) than the control or N_2-treated wines (completed in 17 days), potentially due to the production of yeast fermentation products in the O_2-exposed wines or variations in metal concentrations that led to more favourable MLF conditions. Other factors that influence MLF, including fermentation temperature, wine pH, and alcohol concentrations, did not vary significantly between treatments (AWRI publication #1659).

COLOUR, TANNIN AND SENSORY EFFECTS

The O_2-treated (O_240 and air) wines were significantly lower in total anthocyanin than the control or N_2-treated wines, and were slightly higher in non-bleachable pigments (Figure 1). This suggested that the pigments formed in the presence of higher O_2 were more stable. The wine colour

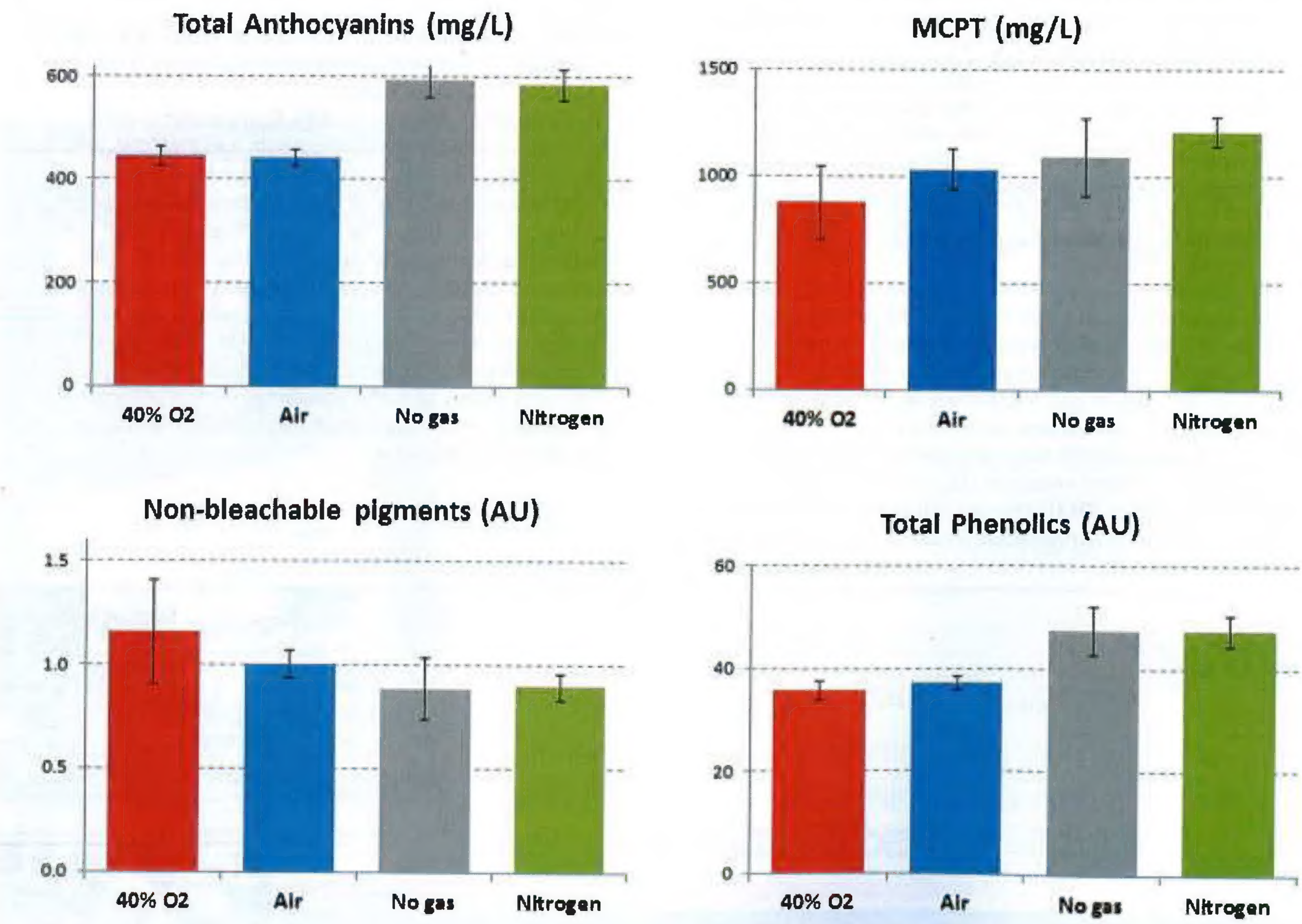

Figure 1. Results of methyl cellulose precipitable tannin (MCPT) and colour measurements made immediately after the end of alcoholic fermentation, showing enhanced and stabilised pigments but lower phenolics and anthocyanins in 40% oxygen and air treatments.

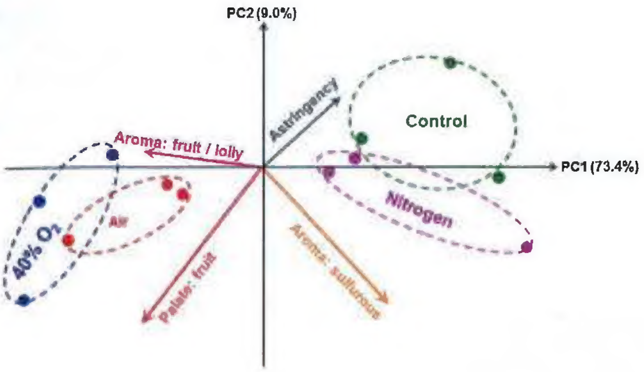

Figure 2. Principal component analysis (PCA) of sensory scores two months after bottling. Wines made with 40% oxygen and air treatments exhibited red fruit characters on aroma and palate, while nitrogen and control treatments were characterised by sulfurous aromas and higher astringency.

density (WCD) remained relatively consistent regardless of fermentation treatment.

Tannin composition was significantly different between the wines produced by the O_2-treated ferments ($O_2$40 and air) and those produced from the control or N_2-treated ferments. The tannins from the $O_2$40 and air wines were less susceptible to depolymerisation reactions (i.e., they were more 'cross linked'), were more coloured and smaller (AWRI publication #1659). Essentially, this means that they resembled aged wine tannins in structure more than young wine tannins, possibly making wines with these sorts of tannins less astringent.

This observation was confirmed by sensory analysis where the $O_2$40 and air treatments scored lowest for bitter and for astringency, while the N_2 treatment scored highest for astringency (Figure 2). These results are also consistent with anecdotal evidence that oxygen diminishes the astringency of red wines.

IMPACT ON METAL CONCENTRATIONS

After bottling, the O_2-treated wines contained significantly lower concentrations of iron, copper and zinc than the control or N_2-treated wines (AWRI publication #1659). The cause of this drop in metal concentrations is unknown, but it could be related to chemical changes in wine components that bind metals, allowing for stronger interactions, or perhaps increased binding by yeast cells. Recent studies have shown the particular importance of metals in the formation of both positive and negative flavour and texture compounds, and on the shelf-life of wine (AWRI publication #1577). The presence of metal ions in wine during storage has been associated with increased concentrations of volatile sulfur compounds responsible for unpleasant aromas as well as more rapid depletion of SO_2, affecting shelf-life. Other effects associated with metals include increased risk of some wine hazes and faster depletion of some positive flavour compounds. Research in this area is continuing at the AWRI and these results suggest that early oxygen exposure in red wines is likely to influence metal-catalysed changes in composition. ▸

IMPACT OF WINE AGEING AND CLOSURE TYPE ON WINE COMPOSITION

After 12 months' bottle ageing of the control and N_2 wines, the colour measures and two tannin compositional characteristics associated with ageing were similar to those of the air and $O_2$40-treated wines after two months of bottle ageing (AWRI publication #1659). This highlights the effect of O_2 during fermentation in producing aged wine-like characteristics. Thus, the level of O_2 exposure during fermentation may also improve the mouthfeel of young red wines by modifying their tannins.

The effect of O_2 exposure during fermentation was also compared with the impact of relatively limited O_2 exposure during bottle-ageing under two different screwcaps: Saranex (Sx), which allows some O_2 ingress, and Saran Tin (ST), which significantly restricts O_2 ingress. The impact of closure type on colour and tannin after 12 months in bottle was greater in the control and N_2-treated wines than the air/$O_2$40 wines (AWRI publication #1659). This may relate to differences in the formation of tannin under each fermentation treatment type. Greater O_2 exposure during fermentation may increase the proportion of oxidised tannins, resulting in the formation of stabilised tannins resistant to further oxidation from O_2 ingress through bottle closures. Thus, the oxidation induced by slight O_2 ingress through the Sx closures was more pronounced in the control and N_2-treated wines than in the air/$O_2$40 wines. Increased O_2 exposure during wine fermentation had a much greater impact on tannin structure in the resulting wine than closure type, and this again highlights the significance of O_2 exposure during fermentation to tannin formation, development and stabilisation.

CONCLUSIONS

Greater oxygen exposure during fermentation produced wines with more 'aged' characteristics in terms of greater hue, fewer anthocyanins, lower tannin concentrations, and smaller tannins with more cross-linked structure. These changes were similar to those induced by 12 months' bottle ageing in wines deprived of oxygen during fermentation. The 40% O_2 and air treatments resulted in wines that were the least bitter and astringent, while the N_2 treatment resulted in wine that was the most astringent. These observations suggest that increased oxygen exposure during winemaking may reduce the need for extended wine ageing, saving winemakers the cost of tannin fining and extended storage. In addition, decreased metal concentrations in O_2-treated wines post-ferment may benefit shelf-life and could lower the risk of reductive aromas. The significantly faster rates of malolactic fermentation in wines that had received O_2 or air treatments might provide a practical tool to assist in the reliable completion of malolactic fermentation. As such, the MLF implications of oxygen exposure are continuing to be investigated.

Research will continue to improve understanding of how oxygen management during processing and fermentation affects areas other than fermentation efficiency. Experiments will explore how oxygenation of ferments can be used to remediate or prevent reductive aromas or to manipulate attributes considered to have a positive impact on wine style. Outcomes from this research represent a significant opportunity for the Australian wine sector to diversify style, manage oxygen exposure effectively and reduce the costs derived from potentially excessive reductive handling of wines.

ACKNOWLEDGEMENTS

This work was supported by Australia's grapegrowers and winemakers through their investment body the Australian Grape and Wine Authority, with matching funds from the Australian Government. The AWRI is a member of the Wine Innovation Cluster. Ella Robinson is thanked for her editorial assistance.

REFERENCES

AWRI publication #1577 Viviers, M.Z.; Smith, M.E.; Wilkes, E. and Smith, P. (2013) Effects of five metals on the evolution of hydrogen sulphide, methanethiol, and dimethyl sulphide during anaerobic storage of Chardonnay and Shiraz wines. J. Agric. Food Chem. 61(50):12,385–12,396.

AWRI publication #1659 McRae, J.M.; Day, M.P.; Bindon, K.A.; Kassara, S.; Schmidt, S.A.; Schulkin, A.; Kolouchova, R. and Smith, P.A. (2014) Effect of early exposure oxygen on red wine colour and tannins. Tetrahedron, DOI 10.1016/j.tet.2014.08.059

Boselli, E.; Di Lecce, G.; Alberti, F. and Frega, N.G. (2010) Nitrogen gas affects the quality and the phenolic profile of must obtained from vacuum-pressed white grapes. LWT - Food Sci. Technol. 43(10):1494-1500.

Cejudo-Bastante, M.J.; Castro-Vazquez, L.; Hermosin-Gutierrez, I. and Perez-Coello, M.S. (2011) Combined effects of prefermentative skin maceration and oxygen addition of must on colour-related phenolics, volatile composition, and sensory characteristics of Airén white wine. J. Agric. Food Chem. 59(22):12,171-12,182.